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पेट्रोलियम एवं इसके उत्पादों की परीक्षण पद्धतियाँ

[पी : 172]

पेट्रोलियम उत्पादों के अतिसूक्ष्म तत्वों का आईसीपी-एईएस विधि से निर्धारण का तरीका

Methods of Test for Petroleum and its Products

[P : 172]

ICP-AES Method for Determination of Trace Elements in Petroleum Products

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Methods of Sampling and Test for Petroleum, its Products, Gaseous Fuels and Lubricants Sectional Committee, PCD 01

FOREWORD

This Indian Standard [P : 172] was adopted by the Bureau of Indian Standards on recommendation of the Methods of Sampling and Test for Petroleum, its Products, Gaseous Fuels and Lubricants Sectional Committee and approval of the Petroleum, Coal and Related Products Division Council.

ICP-AES (Inductively Coupled Plasma — Atomic Emission Spectrometry) also referred to as Inductively Coupled Plasma — Optical Emission Spectrometry (ICP-OES) is an analytical technique used for detection of trace elements. In this technique, element-specific emission spectra produced by radio-frequency inductively coupled plasma are measured by optical spectrometry. Because of its superior detection capabilities and the ability to handle both simple and complex matrices, it has been proven to be a powerful tool for rapid and concurrent determination of trace elements in petroleum products ranging from naphtha to furnace oil including vacuum gas oil and crude oil.

For preparing this test method, inputs have been taken from the relevant ASTM and IP methods, namely, ASTM D5708, ASTM D5185, ASTM D7111 and IP 621, involving Inductively Coupled Plasma — Atomic Emission Spectrometry (ICP-AES).

This method does not purport to address safety problems, if any, associated with its use. It is the responsibility of the user of this method to use appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

If reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 ‘Rules for rounding off numerical values (*revised*)’.

Indian Standard

METHODS OF TEST FOR PETROLEUM AND ITS PRODUCTS

[P : 172]

ICP-AES METHOD FOR DETERMINATION OF TRACE ELEMENTS IN PETROLEUM PRODUCTS

1 SCOPE

1.1 This test method is applicable for determination of trace elements in petroleum products, namely, crude oil, naphtha, middle distillate, vacuum gas oil, residual fuel oils, vacuum residue, lubricating oils and base oils by inductively coupled plasma optical emission spectrometry (ICP-OES).

1.2 The test procedure covers the determination of Al, As, Ba, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, P, K, Na, Si, Ag, S, Sn, Ti, V, and Zn in the concentration range 0.1 mg/kg to 10 mg/kg.

NOTE — The specific elements along with the suggested wavelengths are referred in Table1.Other elements also can be determined based on capability of the instrument.

2 SUMMARY OF TEST METHOD

2.1 Ashing and Fusion Method

A weighed portion of thoroughly homogenized sample of crude oil, vacuum gas oil, residual fuel oil, vacuum residue is combusted and then ashed in a muffle furnace at 575 ± 25°C . The residue is fused with di-lithium tetra borate flux and the fused mixture digested in a solution of tartaric acid and hydrochloric acid. After dilution with water, the solution is aspirated into the plasma of an inductively coupled plasma emission spectrometer and emission radiation of the resonance lines of the elements under analysis is measured, and compared to a curve constructed from standard calibration solution.

2.2 Internal Standard Method

A weighed portion of a thoroughly homogenized naphtha, kerosene, middle distillate, lubricating oils and base oils is diluted tenfold by weight with mixed xylene or other suitable solvent. Standards are prepared in the same manner. A mandatory internal standard is added to the solutions to compensate for variations in test specimen introduction efficiency. The solutions are introduced to the ICP instrument by free aspiration or an optional peristaltic pump. By comparing emission intensities measured with the standards, the concentrations of elements in the test specimen are calculated.

Table 1 Suggested Wavelengths for Various Elements

(*Clause* 1.2, Note)

Sl No.	Element	Wavelength, nm
(1)	(2)	(3)
i)	Aluminum	308.22, 309.27, 396.15
ii)	Arsenic	193.759
iii)	Barium	233.53, 455.40, 493.41
iv)	Boron	249.77
v)	Calcium	315.89, 317.93, 364.44, 422.67
vi)	Chromium	205.55, 267.72
vii)	Copper	324.75
viii)	Iron	238.20, 259.94
ix)	Lead	220.35
x)	Magnesium	279.08, 279.55, 285.21
xi)	Manganese	257.61, 293.31, 293.93
xii)	Mercury	184.950, 194.227, 253.652
xiii)	Molybdenum	202.03, 281.62
xiv)	Nickel	221.65, 227.02, 231.60
xv)	Phosphorus	177.51, 178.29, 213.62, 214.91, 253.40
xvi)	Potassium	766.49
xvii)	Sodium	589.59
xviii)	Silicon	251.61, 288.16
xix)	Silver	328.07
xx)	Sulfur	180.73, 182.62, 182.04
xxi)	Tin	189.99, 242.95
xxii)	Titanium	334.94, 337.28, 350.50
xxiii)	Vanadium	292.40, 309.31, 310.23, 311.07
xxiv)	Zinc	202.55, 206.20, 213.86, 334.58, 481.05

NOTE — These wavelengths are only suggestive. Wavelength of maximum isotopic abundance should be selected for superior sensitivity. If interference is found, alternate wavelength can be selected.

3 SIGNIFICANCE AND USE

The presence of trace elements can have deleterious effect in certain catalytic processes in which hydrocarbons are used as feedstock. This test method is suitable for setting specifications as a quality control tool in process plants. Presence of trace elements beyond threshold limits also causes harm to the environment.

4 REAGENTS AND MATERIALS

Reagent grade chemicals shall be used in all tests. It is intended that all reagents conform to the metal free and the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.1 Ultrapure Water — For dilution of CRM (for preparation of the calibration standards)/samples and for use as blank.

4.2 Hydrochloric Acid — Concentrated, 36 percent (m/m)

4.3 Nitric Acid — Concentrated, 65 percent (m/m), minimum.

4.4 Acid Mixture — Made from 3 parts hydrochloric acid and 1 part nitric acid.

4.5 Dilute Nitric Acid — 1 : 10 mixture of nitric acid and water.

4.6 Internal Standard — Oil soluble cadmium, cobalt or yttrium (or any suitable metal) is required when using internal standardization.

4.7 Multi Element/Organometallic Standards (CRM) — Oil soluble and water soluble standards containing 0.0500 mass percent / 0.100 mass percent of each element as per requirement.

4.8 Dilution Solvent — A solvent that is free of analyses and is capable of completely dissolving standard and samples. In order to match the sample matrix, solvents like mixed xylenes, kerosene, oxylene and ultrapure water and others can be used as dilution solvents.

4.9 Tartaric Acid/Hydrochloric Acid Solution — Dissolve 5 g of tartaric acid in approximately 500 ml of water acidified with 40 ml of hydrochloric acid and dilute to 1 000 ml with water.

4.10 Toluene

4.11 Toluene/Propan-2-ol Mixture — Mix equal volumes of toluene and propan-2-ol.

4.12 Di-Lithium Tetra Borate

4.13 High Purity Argon Gas — Analytical grade, purity 99.995 percent, minimum.

4.14 High Purity Nitrogen Gas — Analytical grade, purity 99.995 percent, minimum.

4.15 High Purity Air — Analytical grade, purity 99.995 percent, minimum.

5 APPARATUS

5.1 Analytical Balance — Minimum capacity 200 g capable of weighing to the nearest 0.1 mg.

5.2 Inductively-Coupled Plasma Atomic Emission Spectrometer — Either a sequential or simultaneous spectrometer is suitable, if equipped with a quartz Inductively Coupled Plasma (ICP) torch and Radio Frequency (RF) generator to form and sustain the plasma.

5.3 Nebulizer — Reduces the possibility of clogging and minimizes aerosol particle effects.

NOTE — A Babington-type high-solids nebulizer is strongly recommended.

5.4 Peristaltic Pump — A peristaltic pump is strongly recommended to provide a constant flow of solution. The pumping speed shall be in the range 0.5 to 3 ml/min. The pump tubing shall withstand at least 6 h exposure to the dilution solvent. Viton tubing is typically used with hydrocarbon solvents, and poly-vinyl chloride tubing is typically used with methyl isobutyl ketone.

5.5 Platinum or Silica Crucible/Dish — 50 ml or 100 ml capacity.

5.6 Hot Plate — With or without magnetic stirring capability.

5.7 Muffle Furnace, Electric — Capable of being maintained at temperatures of 575 ± 25°C and 925 ± 25°C, and preferable having apertures at front and rear to allow passage of a slow, natural draught of air. Ensure that the refractory walls are in good condition, with no loose particles.

5.8 General Laboratory Glassware.

6 SAMPLE PREPARATION

The reliability of analysis is based on representative sample used for testing. In order to achieve homogeneity of sample, the samples shall be thoroughly mixed in their containers immediately prior to testing. Samples which are volatile, shall be cooled in the container with closed lid and manually shaken with vertical strokes for 30 s. Samples which are solid / semi-solids at room temperature, shall be heated to 5°C above the expected pour point, before mixing. The sample mixing shall be done by shaking the container with closed lid manually with vertical strokes or using a high speed shear mixer for 5 min. The chemical decomposition of the sample under preparation for measuring the elements on ICP-AES is mentioned in the procedure.

7 PROCEDURE AND CALCULATION

7.1 Ashing and Fusion Method

This method shall be adopted for samples of crude oil, vacuum gas oil, residual fuel oil and vacuum residue.

7.1.1 *Sample Quantity for Test*

Take sufficient quantity of homogeneous test sample so as to meet the requirements of the analyze with the lowest expected concentration as mentioned in Table 2.

Table 2 Sample Quantity for Test

(*Clause* 7.1.1)

Expected Concentration of Element, mg/kg	Mass of Test Portion, g
0.1 - 3.0	90 - 100
3.1 - 6.0	70 - 90
5.1 - 10.0	50 - 70

7.1.2 Transfer the test portion from the sample container into a previously clean, dry and weighed platinum crucible. Re-weigh the crucible and contents to the nearest 0.1 g and record the mass of sample taken for analysis.

7.1.3 Warm the crucible and contents gently on an electrical heater/bunsen burner until the test portion ignites. Maintain the contents of the crucible at a temperature such that most of the combustible material is removed and only carbon and ash remain in the crucible. If foaming and frothing occur, discard the test portion and add 1 ml to 2 ml of propan-2-ol before heating. If foaming and frothing are not sufficiently reduced, add 10 ml of toluene/propan-2-ol mixture to a further test portion and mix thoroughly. If required to reignite the test portion, ash less filter paper strips can be used.

7.1.4 Place the crucible and its contents in the muffle furnace, preheated to a temperature of 575 ± 25°C. Ensure that the crucible contents are not contaminated with refractory from the furnace walls, as this will contribute to erroneous silicon results. Maintain the muffle furnace at this temperature until all the carbon has been removed and only ash remains.

7.1.5 Cool the crucible to room temperature, add 0.2 g of dilithium tetra borate, and mix it with the ash. Place the crucible and contents in the muffle furnace preheated to a temperature of 925 ± 25 °C for 5 min. Remove the crucible and ensure contact of the dilithium tetra borate with the ash. Once again place the crucible in the muffle furnace and maintain the temperature at 925 ± 25 °C for further 10 min.

7.1.6 Remove the crucible and cool the fusion melt to room temperature. Add 50 ml tartaric acid/hydrochloric acid solution to the crucible and place on the hot plate. Maintain at a moderate temperature without boiling.

7.1.7 Allow the solution to cool and then transfer it in to 100 ml volumetric flask. Wash the crucible several times with water and transfer the washing to the volumetric flask. This washing is essential to ensure that all the fusion melt from crucible is transferred to volumetric flask. Make up to the mark with water and transfer immediately to a 100 ml plastic bottle.

7.1.8 Prepare a blank solution containing only 0.2 g dilithium tetra borate and 50 ml of the tartaric acid/hydrochloric acid solution, diluted to 100 ml in volumetric flask and transfer immediately to another 100 ml plastic bottle.

7.1.9 *Preparation of Calibration Solution*

Prepare 250 mg/l working solution by diluting 25 ml of the 1 000 mg/l standard solution to 100 ml with water. Prepare calibration solution such a way that the calibration solution contains 0.5 mg/l, 1 mg/l and 2 mg/l of each element. Transfer all standards immediately after preparation to 100 ml plastic bottles.

7.1.10 *Setting up the Spectrometer*

a) *General* — Consult and follow the manufacturer's instructions for the operation of the inductively coupled plasma emission spectrometer.

b) *Peristaltic Pump* — If using peristaltic pump, inspect the pump tubing and replaced it, if necessary, before starting each day. Verify the solution uptake rate and adjust it to the desire rate.

c) *ICP Excitation Source* — Ignite the ICP excitation source for at least 30 min before performing an analysis. During this warm-up period, nebulise water through the plasma torch.

d) *Wavelength Profiling* — Perform any wavelength profiling that may be called for in the normal operation of the instrument.

e) *Operation Parameters* — Assign the appropriate operating parameters to the instrument task file so that it is possible to determine the desire elements. Include the following parameters:

    1) element,
    2) wavelength,
    3) background correction points,
    4) inter-element correction factors, and
    5) integration time and three consecutive repeat integrations.

f) *Calibration Curve* — Prepare a three point calibration curve using the blank and working standards at the beginning of each batch of samples.

g) *Analysis of the Test Solution* — Analyze the test portion in the manner as the calibration standards. Rinse the plasma torch between samples by nebulising water for 10 s. If it is found that a test solution gives element content above that of the highest calibration solution, dilute it in the same matrix, namely, blank solution to bring it within the range of the calibration solutions. Analyse one of the calibration standards after every fifth test portion. If any element content is outside 5 percent of the nominal value, make any adjustments to the instrument that are necessary and repeat the calibration.

7.1.11 *Calculation*

Calculate E, the content of the element of interest in mg/kg from the following equation:

$$E = \frac{100\ CD}{M}$$

where,

C = is the element content of interest, in mg/l, as read from the calibration graph or direct read out;

D = is the dilution factor, calculated from the volumes and aliquots taken to produce the test solution; and

M = is the mass of the test portion, in g.

7.2 Internal Standard Method

This method shall be adopted for samples of naphtha, kerosene, middle distillate, lubricating oils and base oils. The internal standard procedure requires that every test specimen solution have the same concentration (or a known concentration) of an internal standard element that is not present in the original specimen. Specimen to specimen changes in the emission intensity of the internal standard element can be used to correct for variations in the test specimen introduction efficiency, which is dependent on the physical properties of the test specimen.

7.2.1 *Preparation of Internal Standard Solution (50 mass ppm)*

Weigh 10 g of 0.500 percent by mass cadmium, cobalt, or yttrium (or any other suitable metal) organo-metallic concentrates into a 1 L volumetric flask and dilute to 1 l with the dilution solvent. Prepare fresh, at least weekly, and transfer this solution into a dispensing vessel.

7.2.2 *Preparation of Test Specimen and Standards*

a) *Blank* — Prepare a blank by diluting the base oil or white oil or matrix solvent ten times by mass with the dilution solvent.

b) *Working Standard*, (10 μg /g) — Weigh 2.0 g of the 0.0500 mass percent multi-element standards into 100 ml volumetric flask. Add 8.0 g of base oil and dilute with 90 g of the dilution solvent. Working standards containing higher or lower concentrations can be prepared as per the requirement. Solutions containing single elements can also be prepared.

c) *Calibration Standard* (0.1, 0.5, 1.0, 2.0 ppm) — Prepare respective calibration standard by appropriate dilution of the working standard.

d) *Check Standards* — Prepare instrument check standards in the same manner as the working standard such that the concentrations of elements in the check standards are similar to the concentrations of elements in the specimens.

e) *Test Specimen* — Weigh 10 g of well homogenized sample into a 100 ml volumetric flask. Add 90 g of dilution solvent to make the test specimen concentration is 10 percent by mass.

f) *Internal Standard* — Add 0.5 ml of internal standard solution to the working standard, check standard and test specimen respectively before dilution solvent and finally make up to 100 g with the dilution solvent. Ensure that the standard or test specimen concentration is 10 percent by mass.

7.2.3 *Calibration*

a) The linear range shall be established once for the particular instrument being used. This is accomplished by running intermediate standards between the blank and the working standard and by running standards containing higher concentrations than the working standard. Analyses of test specimen solutions shall be performed within the linear range of response.

b) *Working Standard with Internal Standard* — At the beginning of the analysis of each batch of specimens, perform a two point calibration consisting of the blank and working standard with internal standard. Use the check standard to determine if each element is in calibration. When the results obtained with the check standard are within 5 percent of the expected concentrations for all elements, proceed with test specimen analyses. Otherwise, make any adjustments to the instrument that are necessary and repeat the calibration. Repeat this procedure with the check standard every five samples.

c) Based on the standard's emission intensities and those of the internal standard, calculate an intensity ratio for each element by the following equation:

$$I\ (Re) = [I\ (e) - I\ (Be)]\ /\ I\ (is)$$

Where,

I (Re) = intensity ratio for element e;

I (e) = intensity for element e;

I (Be) = intensity of the blank for element e; and

I (is) = intensity of internal standard element.

7.2.4 *Procedure and Calculation*

a) *Analysis* — Analyze the test specimen solutions in the same manner as the calibration standards (that is, same integration time, background correction points, plasma conditions, and so forth). Between test specimens, nebulise dilution solvent for 60 s. Calculate elemental concentrations by multiplying the determined concentration in the diluted test specimen solution by the dilution factor. Calculation of concentrations can be performed manually or by computer software when such a feature is available (or as per the manufacturers guidelines).

b) *Quality Control with Check Standard* — Analyze the check standard after every fifth sample, and if any result is not within 5 percent of the expected concentration, recalibrate the instrument and re-analyze the test specimens solutions back to the previous acceptable check standard analysis.

c) *Analysis with Internal Standardization* — Analyze the test specimen solutions and calculate an intensity ratio for each of the elements found in the test specimen solutions using equation (*see* **7.2.3**). From that, intensity ratios, concentrations of the elements can be calculated.

8 EXPRESSION OF RESULTS

Report the element content of each element of interest to the nearest 0.1 mg/kg.

9 PRECISION AND BIAS

9.1 Precision

The precision of this test method is expressed in terms of Relative Standard Deviation (RSD). The RSD shall be 10 percent or better.

9.2 Bias

The method is empirical and depends on various conditions, no statement of bias can be made.

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